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Determinatino of Elemental Concentrations in Fish and Sediments from Rize-Ardesen Area of the East Black Sea

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Some elemental concentrations (K, Ca, Cr, Mn, Fe, Cu, Ni, Zn, Br, Cd, Rb, Sr, Ba, Cs, Zr, Sb, Pb,) of 7 fish species (anchovy, red mullet, grey mullet, sea pike, horse mackerel, whiting and sea-bream), which are largely consumed by human, together with two surface sediment samples from Rize-Ardesen area of the Turkish coast of the east Black Sea have been analyzed by EDXRF spectrometry. Pb was only detected in horse mackerel (2.1 mg/kg) among the muscles of fish species. The results indicated that Mn, Fe, Ni, Cu, Zn and Br were more concentrated in the livers of the fish samples than in muscles, whereas Rb, Sr and Zr concentrations were lower in livers than that in muscles. A positive correlation was found between concentrations of Zn, Cu, Ni and Pb in the sediment and in fish species. The analysis results of the fish samples are compared with those of other marine environment.

Key Words: Fish, Marine sediments, X-Ray fluorescence, Trace elements, Heavy metals.

INTRODUCTION

In aquatic ecosystems, heavy metals have received considerable attention, because of their toxicity effect and accumulation processes in biota[1-5]. Several main and trace elements, in particular heavy metals, are important for the environment. Most of them are essential in organisms in low concentrations, but they may be toxic in high concentrations.

The Black Sea is the largest anoxic marine system. Contaminants such as heavy metals are introduced into the Black Sea through rivers or direct discharge of industrial wastes and agricultural and municipal usage[6]. Moreover, trace and heavy metal pollution of the Black Sea is gradually increasing due to the industrial activities in the region. Although the pollutant levels in the fish organisms are not as high as to have a toxic effect on their life, they could become a potential hazard for human beings according to the

degree of sea food consumption. Therefore, it is found to be important to investigate some elemental concentrations of fish species from the Turkish coast of the east Black Sea. In this study the results of chemical analyses of muscles and livers of some fish species that are largely consumed by human, from Rize-Ardesen area of the east Black Sea together with two surface sediment samples collected from Rize and Ardesen localities are reported.

EXPERIMENTAL

7 Different types of fish species (anchovy, red mullet, grey mullet, sea pike, horse mackerel, whiting and sea-bream) were caught during the year 2005 from the Rize-Ardesen area of the east Black Sea and immediately were stored on ice in an insulated box till transferred to the laboratory. The fishes were dissected into muscle and liver by plastic knifes and after weighing were freeze-dried and then ground to fine particles. Each sample was prepared from at least ten fish product, homogenized in plastic mixer.

The surficial sediment samples (0-4 cm) were collected from Rize and Ardesen localities, in the same period of the fish caught, by using a Lenz Bottom Sampler and were deposited into plastic bags. The samples were dried at 40 ºC for 24 h, crushed and homogenized prior to the analysis.

About 4 g of dry sample powder and 0.9 g WAX, which were homogenized by grinding 5 min using a mixer mill, was pressed into 31 mm diameter pellets by using stainless steel Spex evacuable dies and 25 tons hydraulic press, for quantitative analysis.

The analyses were performed by Spectro IQ EXRF spectrometer. The samples were analyzed for 300 s using an air cooled low power Pd end window X-ray tube (25-50 kV) combined with HOPG crystal for monochromatization and polarization of the primary tube spectrum. A silicon drift detector (SDD) was used to collect the fluorescence radiation from the sample. The resolution of the SDD was better than 175 eV (for MnKα at an input count rate of 10,000 cps). During the measurement the excitation area was flushed with helium gas. The calibration was based on a fundamental parameters model. The calibration curve was calculated by weighed regression. The accuracy of the analytical procedures was checked against the standard reference materials (SRMs)[7]. IAEA's SRMs MA-A1 Copepod, MA-A2 Fish flesh homogenate, H-4 and H-5 and NIST/NBS's SRM 1577, have been analyzed and the analytical results were shown in Table-1. The present results were found to be in confidence interval of SRMs.

All data are presented as concentrations per unit dry weight of the fish species. The analytical results presented are the mean values of three analyses of each sample. Uncertainties are sample standard deviations.

TABLE-1
ELEMENTAL CONCENTRATIONS OF SOME STANDARD REFERENCE MATERIALS IAEA's CRMs MA-A1, MA-A2, H-4 AND H-5 AND NIST/NBS's SRM 1577), OBTAINED BY EDXRF IN THIS STUDY AND THEIR CERTIFIED VALUES (μg/g DRY WEIGHT, UNLESS WHERE INDICATED)

	MA-A1		MA-A2		H – 4		H – 5		1577	
	*	This study	*	This study	*	This study	*	This study	*	This study
K	–	–	–	–	–	–	680(560-800)†	560 ± 41	–	–
Ca	–	–	–	–	186	175 ± 11	21.7 %	20.5 ± 1.5 %	–	–
Mn	–	–	–	–	–	–	30	32 ± 4	–	–
Cu	–	–	–	–	–	–	–	–	193	185 ± 13
Zn	158	155 ± 15	33	36 ± 3	86	91 ± 8	–	–	130	127 ± 10
Rb	–	–	–	–	–	–	24	28 ± 3	18	17 ± 1
Sr	–	–	–	–	–	–	96 (88-105)†	101 ± 10	–	–
Fe	60	63 ± 6	54	58 ± 6	–	–	79 (73-85)†	85 ± 8	270	260 ± 21
Ba	–	–	–	–	–	–	79 (67-92)†	82 ± 8	–	–
Pb	–	–	–	–	–	–	3.1(2.6-3.7)†	2.8 ± 0.3	–	–

*Certified values. Uncertainties are sample standard deviations (1σ and n = 5).
†Values given in parenthesis are confidence interval.

RESULTS AND DISCUSSION

The two surface sediment samples were collected from Rize and Ardesen localities in the same time period. The analysis results of the sediment and fish samples are tabulated in Tables 2 and 3, respectively. The data for fish analysis are presented as concentrations per unit dry weight of the fish species. The correlation between the wet weights and dry weights of the fish species are given in the footnote of the Table-3. Lead was only detected in horse mackerel (2.1 mg/kg), among the muscles of fish species. Liver was always the main accumulating organ of the fish species for heavy

TABLE-2
ANALYTICAL RESULTS (mg/kg, EXCEPT WHERE INDICATED) OF THE BLACK SEA SEDIMENTS TAKEN FROM RIZE AND ARDESEN LOCALITIES

Elements (%)	Rize	Ardesen	Elements (%)	Rize	Ardesen
Na	2.28 ± 0.20	2.30 ± 0.20	Br	55 ± 5	90 ± 8
Ca	0.60 ± 0.05	0.63 ± 0.05	Sr	610 ± 60	565 ± 55
Mn	890.00 ± 86.00	930.00 ± 50.00	Rb	32 ± 3	42 ± 4
Fe	4.20 ± 0.40	2.88 ± 0.27	Zr	285 ± 28	255 ± 25
Ni	36.00 ± 3.00	40.00 ± 3.00	Sb	< 1	< 1
Cu	90.00 ± 8.00	65.00 ± 6.00	Ba	490 ± 45	446 ± 43
Zn	140.00 ± 0.25	230.00 ± 25.00	I	35 ± 3	42 ± 4
Cd	0.85 ± 0.05	0.82 ± 0.05	Pb	7 ± 1	8 ± 0.1

TABLE-3
ANALYTICAL RESULTS OF THE FISH SAMPLES (mg/kg dry weight) FROM RIZE-ARDESEN AREA OF THE EAST BLACK SEA*

(mg/kg dry weight)**	K	Ca	Mn	Cr	Fe	Ni	Cu	Zn	Cd	Rb	Sr	Cs	Zr	Sb	Pb	Ba	Br	I
Muscle																		
Anchovy (*Engraulis encrasicolus* L.)	800± 79	350± 32	5.1± 0.5	5.1± 0.5	30.0± 3.0	4.1± 0.4	7.0± 0.6	46.0± 4.0	2.0± 0.2	3.0± 0.3	75.0± 7.0	1.1± 0.1	45.0± 4.0	1.1± 0.1	≤ 0.5	6.0± 0.5	15.0± 1.5	5.0± 0.4
Red mullet (*Mullus barbatus* L.)	910± 90	410± 40	4.0± 0.4	4.2± 0.4	30.0± 2.5	4.0± 0.4	8.0± 0.8	9.0± 0.9	1.0± 0.1	4.0± 0.4	10.0± 1.0	2.1± 0.2	15.0± 1.4	1.0± 0.1	≤ 0.5	4.0± 0.3	11.0± 1.0	2.0± 0.2
Grey mullet (*Mugil cephalus* L.)	1200± 110	760± 75	5.0± 0.4	3.1± 0.4	20.0± 2.0	1.0± 0.1	5.0± 0.4	37.0± 3.6	1.0± 0.1	4.0± 0.4	72.0± 7.0	3.2± 0.3	35.1± 3.3	1.1± 0.1	≤ 0.5	7.1± 0.7	22.0± 2.0	3.1± 0.3
Sea pike (*Belone belone* L.)	1010± 100	810± 78	3.1± 0.2	5.0± 0.5	27.0± 2.0	2.1± 0.2	6.0± 0.5	9.0± 0.8	1.1± 0.1	5.0± 0.4	15.0± 1.5	2.0± 0.2	18.1± 1.7	1.1± 0.1	≤ 0.5	5.2± 0.5	9.0± 0.8	4.0± 0.4
Horse mackerel (*Trachurus mediterraneus* S.)	860± 85	710± 70	4.2± 0.3	3.2± 0.3	16.0± 1.5	3.2± 0.3	5.0± 0.5	8.0± 0.7	2.1± 0.2	4.0± 0.3	10.0± 1.0	2.1± 0.2	13.0± 1.2	1.0 ± 0.1	2.1± 0.3	5.0± 0.4	8.0± 0.7	3.0± 0.2
Whiting (*Merlangius merlangus* L.)	890± 85	670± 65	4.0± 0.3	4.1± 0.4	14.0± 1.2	1.3± 0.1	5.0± 0.4	6.0± 0.5	1.2± 0.1	3.0± 0.3	6.0± 0.5	3.2± 0.3	11.0± 1.0	1.2± 0.1	≤ 0.5	5.0± 0.4	9.0± 0.8	2.5± 0.2
Sea-bream (*Spicara maenna* L.)	710± 72	590± 58	4.1± 0.4	5.2± 0.5	14.0± 1.3	2.0± 0.2	7.1± 0.6	10.0± 1.0	1.1± 0.1	3.0± 0.3	8.0± 0.7	3.1± 0.3	9.0± 0.8	1.1± 0.1	≤ 0.5	5.1± 0.5	10.0± 1.0	4.2± 0.3
Liver																		
Grey mullet (*Mugil cephalus* L.)	700± 68	520± 50	15.0± 1.2	7.3± 0.6	50.0± 4.0	6.0± 0.6	15.0± 1.0	87.0± 8.0	4.3± 0.4	2.0± 0.2	5.0± 0.5	5.0± 0.5	10.0± 1.0	2.1± 0.2	3.0± 0.3	9.0± 0.8	31.0± 3.0	2.1± 0.2
Whiting (*Merlangius merlangus* L.)	540± 52	900± 89	15.1± 1.1	8.2± 0.7	41.0± 4.0	4.1± 0.4	11.0± 1.0	60.0± 5.0	3.2± 0.3	2.0± 0.2	4.0± 0.4	6.1± 0.6	8.0± 0.7	2.0± 0.2	4.0 ± 0.4	4.0± 0.4	26.0± 2.5	2.0± 0.1

*Mean values of three analyses. **Dry weight/wet weight ratios: Anchovy in muscle = 0.32; Red mullet in muscle = 0.35; Grey mullet in muscle = 0.28; Grey mullet in liver = 0.23; Sea pike in muscle = 0.32; Horse mackerel in muscle = 0.34; Whiting in muscle = 0.30; Whiting in liver = 0.23; Sea-bream in muscle = 0.31.

and trace elements. In the present study concentrations of Mn, Fe, Cu, Ni, Zn, Br, Cd, Cs, Pb and Ba in livers of fish species were higher than those of in muscle, whereas Rb, Sr and Zr concentrations in livers were lower than those in muscle. No significant variations were found for I and Ba concentrations in the liver and muscle. Zn concentrations varied from 6-46 mg/kg dry weight in the muscle, with the highest levels in anchovy (46 mg/kg dry weight) and grey mullet (37 mg/kg dry weight). Cu concentrations varied from 5-8 mg/kg dry weights in the muscle, with highest level in red mullet.

The order of metal concentrations in the sediment samples was Fe > Mn > Zn > Cu > Ni > Pb > Cd (Table-2). Mean concentrations in the muscles of all the fish species except anchovy and grey mullet follow the sequence Fe > Zn > Cu > Mn ≈ Ni > Cd > Pb, while in anchovy and grey mullet the distribution follows the order Zn > Fe > Cu > Mn > Ni > Cd > Pb (Table-3). A positive correlation was found between concentrations of Zn, Cu, Ni and Pb in the sediment and in fish species (muscle and liver).

It can be seen from the Table-3 that, heavy metal concentrations in muscle samples are in agreement with those reported by many studies[8-11] and the limits of tolerance for aquatic organisms were not exceeded[12]. A comparison of some metal concentrations in the muscle of fish species from the Rize-Ardesen area of the east Black Sea with those of reference values are given in Table-4. The results of the anchovy[8,9] and whiting[8], collected in 1997-1998 years and red mullet[10], collected in 1987 from the Turkish coast of the Black Sea, together with that of the groovy mullet, collected from South Africa[11] were included in the Table-4. The trace and heavy element levels of the muscle samples are found to be comparable to those of fish species found previously.

TABLE-4
COMPARISON OF SOME HEAVY AND TRACE METALS IN MUSCLE OF SOME FISH SPECIES

Element (%)	Present study			Reference			
	Anchovy	Red mullet	Whiting	Anchovy [8,9]	Red mullet [10]	Whiting [8]	Groovy mullet [11]
Cr	5.1	4.2	4.1	<0.30-0.84	<0.3	<0.06	4.9-31.6
Mn	5.1	4.0	4.0	1.81-2.99	0.4	2.22-3.56	2.1-14.4
Fe	30	30	14	23.4-61	39.0	46-57	139.3-291.6
Ni	4.1	4.0	1.3	<0.01-2.17		<0.01	-
Cu	7.0	8.0	5.0	2.21-3.39	9.10	1.86-4.54	3.1-14
Zn	46	9.0	6.0	35.7-50.7	11.5	30.2-43.1	51.4-154.3
Cd	2	1.0	1.2	0.10-0.27	<0.1	<0.02	-
Sb	1.1	1.0	1.2	<1.3	-		-
Pb	≤0.5	≤0.5	≤0.5	<0.05-2.51	6.86	<0.05	1.6-20.4

Conclusion

In this study some fish samples from Rize-Ardesen area of the east Black Sea have been analyzed quantitatively for the trace element concentrations using EDXRF spectrometry. The comparison of the trace and heavy element levels of the muscle samples to those of the liver samples indicated that these metals are accumulated in the livers of the fish samples. The trace and heavy element levels of the muscle samples are found to be comparable to those of reference values.

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